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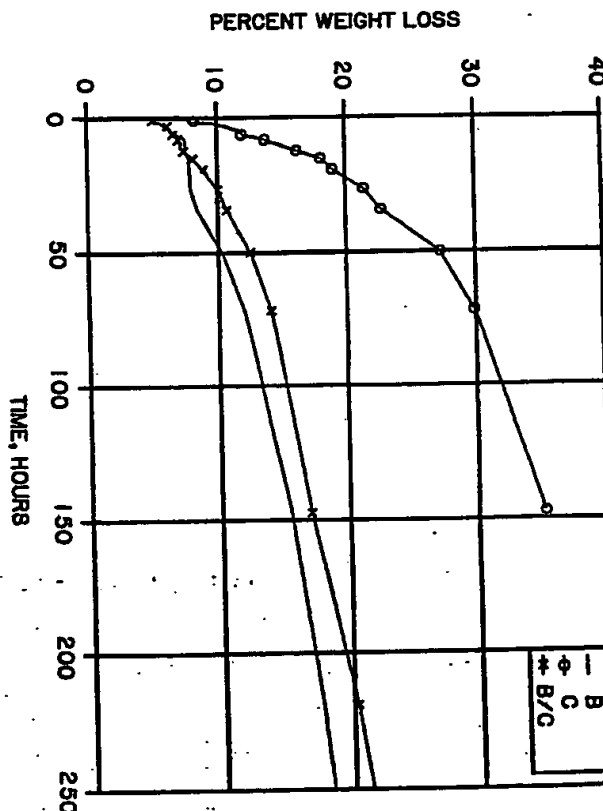
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(54) Title: **SILSESQUIOXANE OLIGOMERS AND OPTICAL GLASS FIBER COATING COMPOSITIONS CONTAINING THE SAME**

(57) Abstract

The present invention is directed to silsesquioxane oligomers substantially free of urethane groups that are the condensation reaction products of a polyhydroxy terminated silsesquioxane with a hydroxy functional ethylenically unsaturated monomer. Photopolymerizable liquid compositions including the oligomer are disclosed. The composition can be used as a single coat or secondary coating for an optical glass fiber which exhibits reduced oxidative degradation and high temperature weight loss. Furthermore, secondary coatings produced therefrom protect conventional primary coatings from these degradative influences.



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SILSESQUIOXANE OLIGOMERS AND OPTICAL GLASS  
FIBER COATING COMPOSITIONS CONTAINING THE SAME

Technical Field

5           This invention is directed to silsesquioxane oligomers and liquid compositions including those oligomers which are suitable as optical glass fiber coatings. The liquid composition can be employed in a single coat system or as a primary or secondary coating  
10   in a two coat system to provide improved resistance to oxidative degradation and high temperature weight loss. A method of making the oligomers is also disclosed.

Background of the Invention

15           Optical glass fibers are conventionally coated with photocured coating compositions. The coating can be a one coat system, or a two coat system comprising a relatively soft primary coating overcoated with a relatively hard secondary coating.

20           Ultraviolet curable coating compositions based on acrylate-terminated polyurethanes are well known for coating optical glass fiber. However, the urethane groups in coatings produced from these compositions break down under the high temperature conditions which optical glass fiber sometimes encounters causing  
25   degradation of the coating and loss of desired mechanical properties. The urethane groups of these coatings can also undergo oxidative degradation at temperatures above 80°C. which leads to the breaking of chemical bonds, weight loss and the resultant breakdown  
30   of the coatings' mechanical properties, making these coatings undesirable for many applications.

          Furthermore, other conventional coatings experience thermal degradation and do not satisfactorily resist temperatures of 125°C. to 150°C. or exposure to  
35   ultraviolet light, as is emitted by the fluorescent lights in common use.

Acrylated polyurethanes based on polyether diols are frequently used in optical fiber coatings, but the polyether linkages in these diols do not provide the best water resistance. To improve the water resistance, efforts have been made to use diols or other polyhydric alcohols which are polyesters or polycarbonates in the formation of the acrylated polyurethane. The acrylated polyurethanes made with these polyesters or polycarbonates possess better water resistance. However, the low modulus needed for the primary coating or single coating of optical glass fiber requires the addition of greater amounts of reactive diluents when these polyester or polycarbonate-based polyurethanes are used, as compared to when polyether polyurethanes are used, to lower the modulus of the coatings. These reactive diluents may contribute to poor adhesion and/or poor water resistance which minimizes the utility of the more water-resistant polyurethanes.

#### Summary of the Invention

The present invention is directed to silsesquioxane oligomers substantially free of urethane groups, a method of making these oligomers, and photopolymerizable liquid compositions including those oligomers that form superior coatings for optical glass fiber. The silsesquioxane oligomers are the condensation reaction products of a hydroxy functional ethylenically unsaturated monomer with a polyhydroxy terminated silsesquioxane. The mole ratio of ethylenically unsaturated monomer: silsesquioxane is about 6:1 to about 1:1, respectively.

The present method of producing the oligomers comprises the step of reacting the silsesquioxane and the ethylenically unsaturated monomer.

The photopolymerizable liquid composition comprises a silsesquioxane oligomer and an ethylenically

unsaturated reactive diluent. These ethylenically unsaturated reactive diluents can contain ether groups which are hydrophilic. In conventional coatings, ether groups lower the water resistance whereas the present composition can utilize ether groups without adversely effecting water resistance.

The present invention also includes liquid acrylate-terminated polyurethane coating compositions that comprise an acrylate-terminated polyurethane, a monoethylenically unsaturated liquid having a glass transition temperature of about 0°C. or less and the silsesquioxane oligomer in an amount of about 2 weight % to about 60 weight %, based on the total weight of the coating composition.

Conventional photoinitiators, light absorbers and stabilizers can also be present.

These compositions can be utilized as single coat glass fiber coatings, primary glass fiber coatings, or secondary glass fiber coatings. The ethylenically unsaturated reactive diluent, and the amount utilized, are selected to obtain the desired softness for the particular application of the coating produced.

Coatings produced from the present oligomers and compositions are relatively thermally stable and exhibit reduced oxidative degradation and reduced high temperature weight loss. Furthermore, when the present compositions are utilized as a secondary glass fiber coating the oxidative degradation and high temperature weight loss of a conventional primary coating overcoated therewith is also reduced and the thermal stability thereof improved. It is presently believed that oxidative degradation is inhibited because the coatings (1) block out light, especially light having an ultraviolet (UV) wavelength, and (2) inhibit diffusion of oxygen into the coatings. Light and heat in the

presence of oxygen are known to accelerate oxidative degradation. Coatings produced from these compositions also exhibit improved water resistance and adhesion.

Brief Description of the Drawings

5

In the drawings,

FIGURE 1 is a graphical representation of percent weight loss as a function of time at 210°C. for coatings B, C and B/C;

10

FIGURE 2 is a graphical representation of percent weight loss as a function of time at 180°C. for coatings B, C and B/C;

FIGURE 3 is a graphical representation of the time required for coatings B,C, and B/C to experience 10 percent weight loss as a function of temperature;

15

FIGURE 4 is a graphical representation of the time required for coatings B,C, and B/C to experience 20 percent weight loss as a function of temperature; and

20

FIGURE 5 is a graphical representation of the time required for coatings A and D to experience 20 percent weight loss as a function of temperature.

Detailed Description of the Preferred Embodiments

25

Although this invention is susceptible to embodiment in many different forms, preferred embodiments of the invention are shown. It should be understood, however, that the present disclosure is to be considered as an exemplification of the principles of the invention and is not intended to limit the invention to the embodiments illustrated.

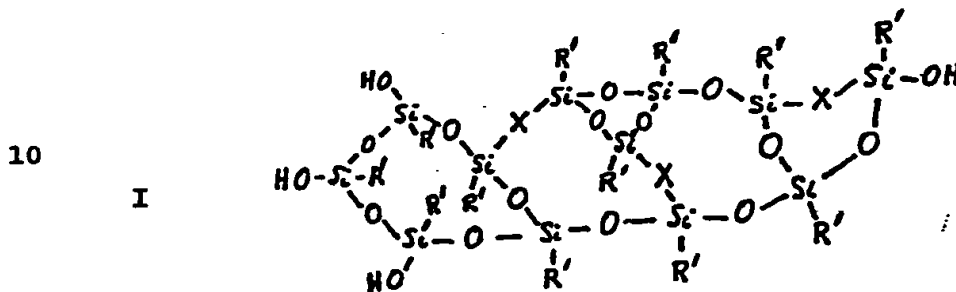
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The silsesquioxane oligomers are the condensation reaction products of a polyhydroxy terminated silsesquioxane with a hydroxy functional ethylenically unsaturated monomer. The oligomers are substantially free of urethane groups, that is, a minor amount of urethane groups can be present which do not adversely affect the performance of the oligomers.

35

These oligomers are admixed with ethylenically unsaturated reactive diluents to produce the present photopolymerizable liquid compositions that are suitable as optical glass fiber coatings.

5 The polyhydroxy terminated silsesquioxane can have the following random structure I:



wherein the R<sup>1</sup>'s are alike or different and are monovalent hydrocarbon groups having 1 to about 10 carbon atoms, preferably a C<sub>1</sub> to about C<sub>5</sub> alkyl group, or a phenyl group, and the Xs are alike or different and are selected from oxygen, siloxane, polysiloxane, or an -O-R<sup>2</sup>-[Si-R<sup>1</sup>]<sub>m</sub>-Y group, wherein R<sup>1</sup> is as described above, R<sup>2</sup> is a C<sub>1</sub> to about C<sub>5</sub> alkylene group, m is 1 or 2, and Y is R<sup>1</sup> or -R<sup>2</sup>-O-. Preferably, the R<sup>1</sup>'s can all be phenyl groups or up to 50% of the R<sup>1</sup>'s can be alkyl groups with the remaining R<sup>1</sup>'s being phenyl groups. X is preferably oxygen.

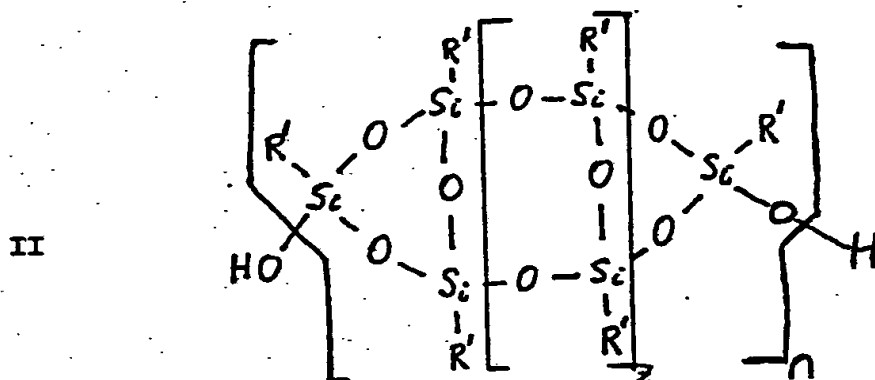
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The polyhydroxy terminated silsesquioxane can also have the following ordered structure II, below,



which is a dihydroxy silsesquioxane:



$R^1$  has been previously described in conjunction with structure I, above,  $n$  is a number having an average value of one to about 3, preferably about 2 and  $z$  is a number having an average value of 1 to about 25, preferably about 1 to about 10.

Typically, both structures I and II are present in samples of the commercial silsesquioxanes.

A minor proportion of a non-silsesquioxane silicone material can be present. Illustrative silicone materials include lower alkyl and/or phenyl substituted siloxanes. Preferably, less than about 30 mole percent of this silicone material is present.

Suitable silsesquioxanes are commercially available. Two illustrative Dow Corning, Midland, MI, products are Z-6018 and 6-2230. The Z-6018 product, according to Dow Corning, contains about 6 weight percent hydroxy functionality per silsesquioxane molecule and has a molar ratio of phenyl groups: alkyl groups bonded directly to the silicon atom of about 2.3:1, respectively. The 6-2230 product contains 5 weight percent hydroxy functionality per silsesquioxane molecule and about 20 mole percent methyl phenyl siloxane and about 80 mole percent of a phenyl silsesquioxane. The molar ratio of phenyl groups to

alkyl groups bonded directly to the silicon atom is about 1.3:1, respectively, for the 6-2230 product. The General Electric commercial product SR-187 can also be utilized.

5           The selection of the hydroxy functional ethylenically unsaturated monomer that is reacted with the polyhydroxy terminated silsesquioxane to produce the oligomer influences the properties of the coating.

10           Hydroxy functional mono- and polyethylenically unsaturated monomers can be utilized with monoethylenically unsaturated monomers being preferred. Monohydroxy functional monomers are preferred albeit a polyhydroxy functional monomer can be present provided it does not cause gelling.

15           The hydroxy functional monomers can be selected from the groups consisting of: hydroxyalkyl acrylates; hydroxyalkyl methacrylates; hydroxyalkyl vinyl ethers; hydroxyalkyl maleates; hydroxyalkyl fumarates; hydroxy functional maleic functional  
20           monomers; and the like. Mixtures can also be utilized. The alkyl group of the above monomers can be C<sub>1</sub> to about C<sub>8</sub> carbon atoms in length.

25           Preferably, the ethylenically unsaturated monomer is selected from the group consisting of hydroxyalkyl acrylates, hydroxyalkyl methacrylates, and mixtures thereof.

30           Illustrative of the hydroxyalkyl acrylates are hydroxyethyl acrylate, hydroxybutyl acrylate, hydroxypentyl acrylate, and the like. The hydroxyalkyl acrylates are presently the preferred ethylenically  
unsaturated monomer. The corresponding methacrylates can also be utilized.

35           Illustrative of the hydroxyalkyl vinyl ethers are hydroxymethyl vinyl ether, hydroxybutyl vinyl ether, and the like.

Illustrative of the hydroxy functional maleic functional monomers are maleic acid half esters, and the like.

5 Illustrative of the hydroxyalkyl maleates are hydroxy propyl monobutyl maleate, hydroxy propyl monoethyl maleate, and the like. The corresponding fumarates are also suitable.

10 The mole ratio of the hydroxy functional ethylenically unsaturated monomer: hydroxy terminated silsesquioxane is about 6:1 to about 1:1, preferably about 3:1 to about 1.5:1. An excess amount of the ethylenically unsaturated monomer can be present which does not react with the silsesquioxane. This excess monomer polymerizes during the cure of the liquid  
15 composition.

Up to about 50 mole percent of the hydroxy functional ethylenically unsaturated monomer can be substituted with a monofunctional alcohol.

20 The number average molecular weight of the oligomer is preferably about 500 to about 7,000, more preferably about 1,000 to about 3,000, daltons.

The term "dalton", in its various grammatical forms, defines a unit of mass that is 1/12th the mass of carbon-12.

25 The viscosity of the oligomer at a temperature of 25°C. is preferably about 100,000 to about 3,000,000, more preferably about 500,000 to about 2,000,000, centipoise (cp).

30 The silsesquioxane oligomer can be produced by the condensation reaction of the polyhydroxy silsesquioxane and the hydroxy functional ethylenically unsaturated monomer. Conventionally, a minor amount of a stabilizer is utilized. An illustrative stabilizer is phenothiazine which is present in an amount less than

about 0.1 weight percent based on the total weight of the silsesquioxane, monomer and stabilizer.

During the condensation reaction of the silsesquioxane and the hydroxy functional ethylenically unsaturated monomer, the silsesquioxane can also self-condense, i.e., react with itself, thus increasing the number average molecular weight of the oligomer produced. The relative rates of the condensation and self-condensation reactions can be optionally controlled by a catalyst. Illustrative catalysts include tetraisopropyl titanate and dibutyltin dilaurate, both of which shift the reaction to favor the condensation reaction. The molecular weight of the oligomer can influence the modulus and other properties of coatings produced from the oligomer.

The reaction is conducted in a suitable vessel such as a 4-neck flask fitted with a thermometer, a controllable heat source, a Dean-Stark tube fitted with a condenser and a sparge tube.

The reactants, i.e., the silsesquioxane, hydroxy functional monomer and stabilizer, are introduced into the vessel and the temperature elevated to melt the reactants. After melting, dry air is bubbled through the liquid reactants via the sparge to inhibit the free radical polymerization of the hydroxy functional monomer.

The temperature is increased until distillate begins to collect in the condenser. Thereafter, the reactants are maintained at approximately this temperature, even though temperature variations can be utilized to achieve a complete reaction. The temperature is controlled to produce a distillate that is primarily water although some impurities can be present. The condensation reaction continues until the desired viscosity is achieved.

The polyhydroxy silsesquioxane can be dissolved in up to about 10 weight percent of a diluent, e.g., phenoxy ethyl acrylate, prior to the addition of the unsaturated monomer. The use of such a diluent  
5 reduces the viscosity of the silsesquioxane oligomer to about 20,000 cp.

The resultant oligomer can be admixed with an ethylenically unsaturated reactive diluent to produce a liquid composition that is suitable as an optical glass  
10 fiber coating.

The ethylenically unsaturated reactive diluent can impart additional flexibility and a lower modulus to coatings produced from the composition. Preferably, the glass transition temperature ( $T_g$ ) of homopolymers  
15 produced from the ethylenically unsaturated reactive diluent is about 0°C. or less for compositions utilized to produce single coat coatings or primary coatings. However, if the composition is utilized as a secondary coating, the  $T_g$  of the ethylenically unsaturated  
20 reactive diluent can be about 25°C. or higher.

The term "glass transition temperature", in its various grammatical forms, is defined as the temperature at which a homopolymer of the referenced material changes from a vitreous state to a plastic  
25 state.

The ethylenically unsaturated reactive diluents can be mono- or polyethylenically unsaturated with monoethylenically unsaturated reactive diluents presently being preferred.

30 Illustrative ethylenically unsaturated reactive diluents are selected from the group consisting of acrylates, methacrylates, vinyl monomers and mixtures thereof, e.g., 2-phenoxyethyl acrylate, octyl/decyl acrylate (an admixture of octyl acrylate and decyl  
35 acrylate), hexane diol diacrylate, hexane diol

dimethacrylate, vinyl ethers, triethylene glycol divinyl ether, the like and mixtures thereof.

The weight ratio of silsesquioxane oligomer:  
ethylenically unsaturated reactive diluent is about 20:1  
5 to about 1:1, respectively, preferably about 10:1 to  
about 4:1, respectively.

The liquid composition can be produced by  
admixing the oligomer and ethylenically unsaturated  
reactive diluent in a suitable vessel until substantial  
10 homogeneity is achieved.

The present liquid compositions also are  
exemplified by acrylate-terminated polyurethane coating  
compositions (the acrylated polyurethane compositions)  
comprising the silsesquioxane oligomer in an amount  
15 preferably in the range of about 2 to about 60 weight  
percent based on the total weight of the acrylated  
polyurethane composition, the monoethylenically  
unsaturated liquid having a  $T_g$  of about 0°C. or less and  
an acrylate-terminated polyurethane.

The silsesquioxane oligomer has been  
20 previously described and is more preferably present in  
an amount in the range of about 5 to about 55, most  
preferably about 8 to about 30 weight percent based on  
the total weight of the acrylated polyurethane  
25 composition.

The monoethylenically unsaturated liquids are  
diluent which are normally acrylate ethers, typically  
ethoxyethoxyethyl acrylate and phenoxyethyl acrylate.  
The proportion of the monoethylenically unsaturated  
30 liquid is determined by the amount needed to provide  
coating viscosity, but these ethers tend to introduce  
sensitivity to water, so it is desired to minimize the  
need for such diluents.

The acrylate-terminated polyurethanes are  
35 usually diacrylates of isocyanate-terminated oligomers

made from a polymeric diol or polymeric diamine, the acrylate-terminated polyurethane having a molecular weight in the range of about 2000 to about 8000 daltons. The polyurethane preferably contains an average of about 4 to about 12, more preferably about 5 to about 10 urethane and/or urea groups per molecule. Although the acrylated polyurethanes used herein are generally diacrylates, they have an average acrylate functionality slightly below or above 2.0. Acrylate functionality in excess of an average of two can be obtained in various ways, as when a monohydric polyacrylate is used to cap the polyurethane, or when a small proportion of triol is used in the formation of the polyurethane.

The acrylate-terminal group is conventionally introduced with a urethane linkage by the reaction of the isocyanate group with an hydroxy group supplied by a monohydric acrylate, typically 2-hydroxyethyl acrylate. Alkyl acrylates of about  $C_2$  to about  $C_4$  are suitable for use herein as are polyacrylates, such as glyceryl diacrylate.

The wavelength of the light utilized to cure the liquid composition of the present invention can vary depending upon the photoinitiator selected. In present practice, the light utilized is usually in the ultraviolet range which extends from about 200 to about 400 nanometers (nm). However, light of a longer wavelength, e.g., light having a wavelength of up to 600 nm, preferably up to about 520 nm, can be utilized.

The liquid composition includes a photoinitiator when it is to be cured and can be cured in an air atmosphere. Preferred photoinitiators are aryl ketones, e.g., benzophenones, acetophenone derivatives such as diethoxy acetophenone, benzoin, benzoin alkyl ethers, benzil ketal, thioxanthenes, and

the like. Illustrative is Irgacure 651, commercially available from Ciba-Geigy Corp., Ardsley, NY.

5 A suitable light absorber is UV 416, which is 2-hydroxy-4-acrylyloxyethoxy benzophenone, commercially available from American Cyanamid Co., Wayne, NJ.

A suitable antioxidant is Irganox 1076, which is a hindered phenolic, commercially available from Ciba-Geigy Corp., Ardsley, NY.

10 Conventional stabilizers such as hindered amines which provide ultraviolet stability for the cured composition can be present in amounts less than about 1 weight percent. Illustrative stabilizers include bis(2,2,6,6,-tetramethyl-4-piperidiny) sebacate which is commercially available from Ciba-Geigy Corp.,  
15 Ardsley, NY, under the trade designation Tinuvin 770 and thiodiethylene (3,5-di-tert-butyl-4-hydroxy) hydrocinnamate, also commercially available from Ciba-Geigy Corp.

20 The oligomer and ethylenically unsaturated reactive diluent can be present in the liquid composition in an amount in the range of about 90 to about 98, preferably about 96 to about 98, weight percent of the total weight of the liquid composition.

25 The photoinitiator can be present in the liquid composition in a range of about 0.5 to about 10, preferably about 2 to about 6, weight percent based on the total weight of the liquid composition.

30 The light absorbers, antioxidants and stabilizers can be present in the liquid composition in an amount up to about 3 weight percent based on the total weight of the liquid composition.

As a contrast with this invention, especially the acrylated polyurethane compositions, we have attempted to obtain useful results by adding  
35 3-methacryloxypropyl trimethoxy silane, a known adhesion



promoter, in small amounts. This agent improves adhesion slightly, but it reduces cure speed. Thus, when used in an amount of 0.5 weight %, it provides some improved adhesion, but the cure speed is significantly reduced. Larger amounts used in an effort to further improve adhesion cause even greater reductions in cure speed, and they also increase the coating's propensity towards water absorption. Thus, this invention provides significant improvement, as documented below, where a prior art additive known to us is not effective.

The present liquid composition can be applied to glass fibers utilizing conventional processes. Typically, the thickness of the applied coating is about 3 mils.

The following Examples are presented by way of illustration and not limitation.

EXAMPLE 1:      Preparation of The  
                 Silsesquioxane Oligomer

The silsesquioxane, the 2-hydroxyethyl acrylate and the phenothiazine stabilizer were introduced into a one liter, 4 neck flask fitted with a thermometer, a controllable heat source, a Dean-Stark tube fitted with a condenser and a sparge tube. The reactants and the proportions utilized thereof are presented in TABLE I, below.

The contents of the flask were heated and melted prior to the insertion of the sparge tube. Dry air was bubbled through the melted reactants.

Heating was continued. At about 160°C., distillate began to collect. Heating was maintained until about 18.5 milliliters of water was distilled. The final temperature of the reactants was 167°C. The temperature of the reactants was maintained at a level at which distillation continued during the reaction.

The resultant distillate was an azeotrope containing minor amounts of 2-hydroxyethyl acrylate and other impurities.

5

TABLE I

## SILSESQUIOXANE OLIGOMER

<u>Reactants</u>	<u>Weight (grams)</u>
Z-6018 <sup>1</sup>	576.3
2-hydroxyethyl acrylate	239.9
10 Phenothiazine stabilizer	0.7

<sup>1</sup> A hydroxy terminated silsesquioxane based polymer commercially available from Dow Corning.

15

EXAMPLE 2: Liquid Compositions of the Present Invention

Aliquots of the silsesquioxane oligomer of EXAMPLE 1 were utilized to make liquid compositions. The constituents, and proportions thereof, of these liquid compositions are presented in TABLE II, below. The liquid compositions were prepared by admixing the constituents in a suitable vessel until the admixture was substantially homogeneous.

25

TABLE II

## LIQUID COMPOSITIONS

<u>Constituents</u>	<u>Composition, weight (grams)</u>	
	A	B
30 Oligomer <sup>1</sup>	83.5	83.5
Phenyoxyethyl acrylate	12.0	12.0
Irgacure 651 <sup>2</sup>	3.0	3.0
Light absorber <sup>3</sup>	- -	0.7
Antioxidant <sup>4</sup>	- -	0.8

35

<sup>1</sup> The silsesquioxane oligomer of EXAMPLE 1 was utilized.

<sup>2</sup> A photoinitiator commercially available from Ciba-Geigy Corp., Ardsley, NY.

5 <sup>3</sup> UV 416, commercially available from American Cyanamid Co., Wayne, NJ.

<sup>4</sup> Irganox 1076, commercially available from Ciba-Geigy Corp., Ardsley, NY.

10 A comparison was made of the high temperature weight loss, using thermographic analysis, for samples of coatings prepared from the present compositions of EXAMPLE 2 (A and B), a conventional primary coating (C) available from DeSoto, Inc., Des Plaines, IL, under the  
15 designation DeSolite 950-701, a coating (B/C) of the above-identified conventional primary coating (C) overcoated with a secondary coating prepared from composition (B) of EXAMPLE 2 and a conventional secondary coating (D) available from DeSoto, Inc., under  
20 the designation DeSolite 3471-2-21. The results of the comparison are presented in TABLE III, below.

The thermographic analysis was conducted by drawing down a 3 mil thick coating on a previously weighed glass plate using a Bird bar, commercially  
25 available from Pacific Scientific, Silver Springs, MD. The coating was cured using a "D" lamp, from Fusion Curing Systems, Rockville, MD. The "D" lamp emits radiation having a wavelength of about 200 to about 470 nanometers with the peak radiation being at about 380  
30 nanometers and the power output thereof is about 300 watts per linear inch. Coating A and coating D were cured at 0.8 Joules/centimeter squared ( $J/cm^2$ ). Coating B and coating C were cured at 1.5  $J/cm^2$ . To produce coating B/C, the primary coating (C) was cured at 0.5

J/cm<sup>2</sup> and the secondary coating (B) was cured at 1.75 J/cm<sup>2</sup>.

The temperatures of two ovens having air flow were equilibrated at a temperature of either 210°C. or 180°C. The coated glass plate was weighed prior to being placed in the oven and the weight of the uncoated glass plate subtracted therefrom to obtain the weight of the unheated coating. The coated glass plate was then placed in an oven and maintained therein for the specified time period. At the end of this time period, the coated glass plate was removed from the oven, reweighed and replaced into the oven. The percent weight change (% wt. change) was calculated using the following equation:

$$1: \frac{G - E}{F} \times 100 = \% \text{ wt. change}$$

Wherein:

E = Weight [grams (g)] of the glass plate and unheated coating;

F = Weight (g) of the unheated coating; and

G = Weight (g) of the glass plate and heated coating.

Three samples of each coating were compared, the average of which is presented in TABLE III.

TABLE III

HIGH TEMPERATURE WEIGHT LOSS COMPARISON

30

Temperature : 180°C.		<u>Coatings A &amp; D (% wt. loss)</u>	
<u>Time (hours)</u>		<u>A</u>	<u>D</u>
72		8.3	28.6
405		13.0	42.8
526		13.5	46.8

35

18

Temperature : 210°C.

Time (hours)

	44	10.4	35.0
	162	14.7	44.8
5	292	18.3	52.6

Temperature : 210°C.

Time (hours)Coatings B, C & B/C (% wt. loss)

		<u>B<sup>1</sup></u>	<u>C<sup>2</sup></u>	<u>B/C<sup>3</sup></u>
	1	5.3	8.2	5.0
10	3	8.8	11.8	6.2
	6	6.8	11.9	6.6
	8	7.5	13.7	7.0
	12	7.5	16.2	7.4
	15	7.8	18.1	8.1
15	19	7.4	19.0	8.9
	26	7.9	21.4	10.0 <sup>4</sup>
	34	8.4	22.7	10.7
	50	10.3	27.3	12.5
	72	12.0	29.9	14.1
20	147	15.4	35.3	17.0
	219	17.6	39.6	20.3
	291	19.3	42.6	22.8
	339	20.7	45.1	24.4
	459	22.5	49.7	28.4
25	531	25.6	53.5	30.6

Temperature : 180°C.

Time (hours)

	1	4.2	8.1	4.7
30	3	5.8	10.2	5.7
	6	5.8	10.9	5.8
	8	5.4	11.2	5.8
	12	5.5	11.9	6.0
	15	6.0	13.1	6.4
35	19	5.6	13.3	6.3

19

	26	6.1	15.7	6.7
	34	6.3	16.8	7.0
	50	6.7	19.9	7.5
	72	7.3	21.2	9.0
5	147	7.8	25.9	11.4
	219	9.1	28.2	12.7
	291	9.9	31.1	14.6
	339	10.8	32.7	15.1
	459	11.2	35.5	16.2
10	531	12.5	38.3	17.3
	675	14.8	NA <sup>5</sup>	19.6

- 
- 15    <sup>1</sup> Coating B yellowed at 219 hours at 210°C.  
<sup>2</sup> Coating C browned at 26 hours at both temperatures.  
<sup>3</sup> Coating B/C browned at 26 hours at 210°C. and at 531 hours at 180°C.  
<sup>4</sup> The secondary coating B delaminated from primary  
20    coating C, exposing the same, for one of the three samples tested. Testing continued after delamination.  
<sup>5</sup> NA = Not available.

25            The results of the comparison indicate that coating C (the conventional primary coating alone) and coating D (the conventional secondary coating alone) both lost a significant amount of weight in a relatively short time period at both temperatures and would not be suitable for high temperature applications. However,  
30    coatings A and B (the coatings of the present invention) and coating B/C [the conventional primary coating (C) overcoated with the coating of the present invention as a secondary coating (B)], which are far superior to coatings C and D, are suitable for high temperature  
35    applications because of low weight loss which also

indicates reduced oxidative degradation. Furthermore, as coating B/C illustrates, the coating of the present invention when utilized as a secondary coating protects the primary coating from high temperature weight loss.

5 A comparison of coating A and coating B shows that there is no significant difference between the percent weight loss for them. This indicates that the present coating compositions, regardless of whether light absorbers or antioxidants are utilized, are thermally stable.

10 The results are graphically represented in FIGURES 1-5.

FIGURE 1 shows that at a temperature of 210°C. coating B exhibits less weight loss and therefore is superior to coating B/C which is superior to coating C.

15 FIGURE 2 shows that at a temperature of 180°C. coating B exhibits less weight loss and therefore is superior to coating B/A which is superior to coating C.

FIGURE 3 was generated by determining the time required for each coating to experience a 10 percent weight loss at 210°C. and 180°C. These temperatures were converted to degrees Kelvin and the time versus temperature plotted on a semi-log scale. This Figure also shows that coatings utilizing the present invention (B and B/C) exhibit a significant reduction in thermal weight loss as compared to coatings not utilizing the present invention. Furthermore, conventional primary coatings overcoated with the present invention also exhibit a reduction in thermal weight loss (B/C).

20 25 30 FIGURES 4 and 5 were generated by determining the time required for each coating to experience a 20 percent weight loss at the indicated temperatures. These temperatures were converted to degrees Kelvin and the time versus temperature plotted on a semi-log scale.

FIGURES 4 and 5 graphically illustrate the superiority of the present coating compositions, as represented by coating A and coating B, as compared to coating B/C and especially as compared to a conventional primary coating C and conventional secondary coating D.

EXAMPLE 3:      Preparation of the  
                  Acrylate-Terminated Polyurethane

The acrylate-terminated polyurethane was conventionally made by reacting 2 moles of 2-hydroxyethyl acrylate with 1 mole of a polyoxytetramethylene glycol having a number average molecular weight of 650 daltons and 1 mole of the isocyanate-terminated reaction product of two molar proportions of methylenebis 4-cyclohexyl isocyanate with one molar proportion of polyoxytetramethylene glycol having a number average molecular weight of 1000 daltons. This urethane-forming reaction was carried out in ethoxyethoxyethyl acrylate in the presence of 1 weight % of dibutyltin dilaurate catalyst for the reaction.

EXAMPLE 4:      Preparation of The Silsesquioxane  
                  Oligomer

The silsesquioxane oligomer was prepared by placing in a 1 liter, 4-neck flask 576.3 grams of Dow Corning's product Z-6018, described previously, dissolved in 7.2 weight percent, based on the total weight of the composition, of phenoxy ethyl acrylate. To the flask were added 239.9 grams of 2-hydroxyethyl acrylate and 0.7 grams of phenothiazine stabilizer. The flask was fitted with a thermometer and a Dean-Stark tube fitted with a condenser so that distillate could be collected. The contents of the flask were heated until



all of the ingredients melted and then a sparge tube was added and dry air was bubbled through the liquid.

Heating was continued, and at 162°C., distillate began to collect. Heating was continued until 18.5 ml. of water was distilled from the flask. The final temperature was 167°C. The refractive index of the distillate was found to vary from 1.347 to 1.359 during the course of the distillation. The deviations from the refractive index value for pure water are attributed to small amounts of 2-hydroxyethyl acrylate and other impurities that are present in the azeotrope.

The product produced above was cooled and packaged for subsequent use. The refractive index was 1.5175, the density was 10.4 pounds per gallon, and the Brookfield viscosity was 19,300 centipoises (measured with a #6 RV bob at 25°C.)

EXAMPLE 5: Comparison of Various Acrylated Polyurethane Compositions and of Conventional Acrylate-Terminated Polyurethane Containing Composition

Compositions H to K were prepared by admixing their respective components of TABLE IV in suitable vessels.

TABLE IV  
COATING COMPOSITIONS

Component	Composition (weight percent)				
	H	I	J	K	L
Polyurethane <sup>1</sup>	95.0	90.0	85.0	43.6	100
Silsesquioxane					
Oligomer <sup>2</sup>	5.0	10.0	15.0	50.0	--
2-PEA <sup>3</sup>	--	--	--	6.1	--
DC 57 <sup>4</sup>	--	--	--	0.3	--

<sup>1</sup> A polyurethane admixture containing 70.5 weight percent of the acrylate-terminated polyurethane of EXAMPLE 3, 24.5 weight percent ethoxyethoxyethyl acrylate, 4 weight percent hydroxycyclohexyl phenyl ketone (Irgacure 184 from Ciba-Geigy, Ardsley, NY) as the photoinitiator, and 1 weight percent of conventional stabilizers (the stabilizers are optional).

<sup>2</sup> The diacrylate (prepared as described in EXAMPLE 4) of a commercial silsesquioxane obtained from Dow Corning under the trade designation Z-6018.

<sup>3</sup> 2-phenoxyethyl acrylate.

<sup>4</sup> A polymethyl siloxane flow control agent which helps to compatibilize the components of the composition with one another.

Coating Compositions H to L were then tested for dry adhesion and wet adhesion and Compositions K and L were also tested for water absorption and water extractables. The results of these test are presented in TABLE V.

TABLE V  
TEST RESULTS

Test	Composition				
	H	I	J	K	L
	Results				
Dry adhesion (g)	17.9	21.8	24.9	190	16.1
Wet adhesion (g)	5.5	8.5	5.5 <sup>1</sup>	14.0	4.9
Water					
Absorption (%)	--	--	--	0.1	2.4
Water					
Extractables (%)	--	--	--	2.5	3.4

<sup>1</sup> This value is not an expected result. The test was not repeated to ensure the value's accuracy and value is concluded to represent experimental error.

To determine the dry and wet adhesion of a film to glass, films were prepared by drawing down 3 mil coatings on glass plates using the Bird bar. The coatings were cured using the "D" lamp.

The films were then conditioned at a temperature of  $23 \pm 2^{\circ}\text{C}$ . and a relative humidity to  $50 \pm 5\%$  for a time period of 7 days. The film to be tested for wet adhesion was further conditioned at a temperature of  $23 \pm 2^{\circ}\text{C}$ . and a relative humidity of 95% for a time period of 24 hours. A layer of a polyethylene/water slurry was applied to the surface of the further conditioned film to retain moisture. The film which was not further conditioned was utilized for the dry adhesion test.

The test is performed utilizing an apparatus including a universal testing instrument, e.g., an Instron Model 4201 commercially available from Instron Corp., Canton, MA, and a device, including a horizontal support and a pulley, positioned in the testing instrument.

After conditioning, sample specimens that appeared to be uniform and free of defects were cut in the direction of the draw down. Each specimen was 6 inches long and one inch wide and free of tears or nicks. The first one inch of the length of each specimen was peeled back from the glass plate. The plate was secured to the horizontal support with the affixed end of the specimen adjacent to the pulley. A wire was attached to the peeled-back end of the specimen, run parallel to the specimen and then run through the pulley in a direction perpendicular to the specimen. The free end of the wire was clamped in the upper jaw of the testing instrument which was then activated at a 10 inch per minute strain rate. The test

was continued until the average force value becomes relatively constant.

5 The test results indicated that the compositions of the present invention (compositions H to K) exhibit superior dry and wet adhesion as compared to a conventional composition L. Furthermore, the properties improve as the percent silsesquioxane oligomer increases.

10 To determine the water resistance a 10 mil draw-down of the composition was made on a glass plate utilizing the Bird bar. The composition was cured utilizing the "D" lamp. Three test samples each having dimensions of 1/2" x 1" x 1/2" were cut from the cured coating. Each sample was weighed utilizing an  
15 analytical balance to obtain weight measurement M and then immersed in separate containers of deionized water. After a time period of 24 hours, the samples were removed from the water; blotted to remove excess water on the surface and reweighed to obtain weight  
20 measurement N. The samples were then placed in aluminum pans and maintained therein at ambient conditions, i.e., ambient temperature (about 20 - 30°C.) and ambient humidity, for a time period of 120 hours. The samples were then reweighed to obtain weight measurement Q. The  
25 following formulations are utilized to calculate the water absorption and the extractables.

$$(I) \text{ \% water absorption} = [(N - M)/M] \times 100$$

$$(II) \text{ \% extractables} = [(Q - M)/M] \times 100$$

Commercial requirements suggest that the  
30 difference between the percent water absorption and the percent extractables can be as high as about 1.5. The present coating composition provides coatings which exhibit water resistance at about this maximum acceptable value.

The test results indicate that the Composition K of the present invention has superior water absorption and water extractable properties as compared to conventional Composition L.

5 This invention has been described in terms of specific embodiments set forth in detail, but it should be understood that these are by way of illustration only and that the invention is not necessarily limited thereto. Modifications and variations will be apparent  
10 from the disclosure and may be resorted to without departing from the spirit of the invention, as those skilled in the art will readily understand. Accordingly, such variations and modifications of the disclosed products are considered to be within the  
15 purview and scope of the invention and the following claims.

WE CLAIM:

1. A silsesquioxane oligomer substantially free of urethane groups comprising the condensation reaction product of a hydroxy functional ethylenically unsaturated monomer with a polyhydroxy terminated silsesquioxane, the ethylenically unsaturated monomer: silsesquioxane mole ratio being about 6:1 to about 1:1, respectively.
2. The oligomer in accordance with claim 1 wherein the ethylenically unsaturated monomer: silsesquioxane mole ratio is about 3:1 to about 1.5:1, respectively.
3. The oligomer in accordance with claim 1 that has a number average molecular weight of about 500 to about 7,000 daltons.
4. The oligomer in accordance with claim 1 that has a number average molecular weight of about 1,000 to about 3,000 daltons.
5. A silsesquioxane oligomer substantially free of urethane groups comprising the condensation reaction product of a polyhydroxy terminated silsesquioxane with a monohydroxy functional ethylenically unsaturated monomer, the ethylenically unsaturated monomer: silsesquioxane mole ratio being about 3:1 to about 1.5:1, respectively.
6. The oligomer in accordance with claim 5 that has a number average molecular weight of about 500 to about 7,000 daltons.
7. The oligomer in accordance with claim 5 that has a number average molecular weight of about 1,000 to about 3,000 daltons.
8. A photopolymerizable liquid composition suitable as an optical glass fiber coating composition comprising:

(a) a silsesquioxane oligomer substantially free of urethane groups that is the condensation reaction product of a hydroxy functional ethylenically unsaturated monomer with a polyhydroxy terminated silsesquioxane, the ethylenically unsaturated monomer: silsesquioxane mole ratio being about 6:1 to about 1:1, respectively; and

(b) an ethylenically unsaturated reactive diluent.

9. The liquid composition in accordance with claim 8 wherein the ethylenically unsaturated reactive diluent has a  $T_g$  of about 0°C. or less.

10. An optical glass fiber coated with a cured coating of the liquid composition of claim 9.

11. The liquid composition in accordance with claim 8 wherein the ethylenically unsaturated reactive diluent has a  $T_g$  of about 25°C. or more.

12. An optical glass fiber coated with a primary coating and then overcoated with a cured coating of the composition of claim 11.

13. The liquid composition in accordance with claim 8 wherein the weight ratio of silsesquioxane oligomer: ethylenically unsaturated reactive diluent is about 20:1 to about 1:1, respectively.

14. The liquid composition in accordance with claim 8 wherein the weight ratio of silsesquioxane oligomer: ethylenically unsaturated reactive diluent is about 10:1 to about 4:1, respectively.

15. A photopolymerizable liquid composition suitable as an optical glass fiber coating composition comprising:

(a) a silsesquioxane oligomer substantially free of urethane groups that is the condensation reaction product of a hydroxy functional ethylenically unsaturated monomer with a polyhydroxy terminated

silsesquioxane, the ethylenically unsaturated monomer: silsesquioxane mole ratio being about 3:1 to about 1.5:1, respectively; and

5 (b) an ethylenically unsaturated reactive diluent, the weight ratio of silsesquioxane oligomer: reactive diluent being about 20:1 to about 1:1, respectively.

10 16. The liquid composition in accordance with claim 15 wherein the ethylenically unsaturated reactive diluent has a  $T_g$  of about 0°C. or less.

17. An optical glass fiber coated with a cured coating of the liquid composition of claim 16.

15 18. The liquid composition in accordance with claim 15 wherein the ethylenically unsaturated reactive diluent has a  $T_g$  of about 25°C. or more.

19. An optical glass fiber coated with a primary coating and then overcoated with a cured coating of the composition of claim 18.

20 20. A photopolymerizable liquid coating composition comprising:

(1) an acrylate-terminated polyurethane;

(2) a monoethylenically unsaturated liquid having a glass transition temperature of about 0°C. or less; and

25 (3) a silsesquioxane oligomer that is the condensation reaction product of a hydroxy functional ethylenically unsaturated monomer with a polyhydroxy terminated silsesquioxane, the ethylenically unsaturated monomer:silsesquioxane mole ratio being about 6:1 to  
30 about 1:1, respectively, the proportion of said silsesquioxane oligomer being in the range of about 2% to about 60% of the weight of said coating composition.

21. A liquid coating composition as recited in claim 20 in which said silsesquioxane oligomer is



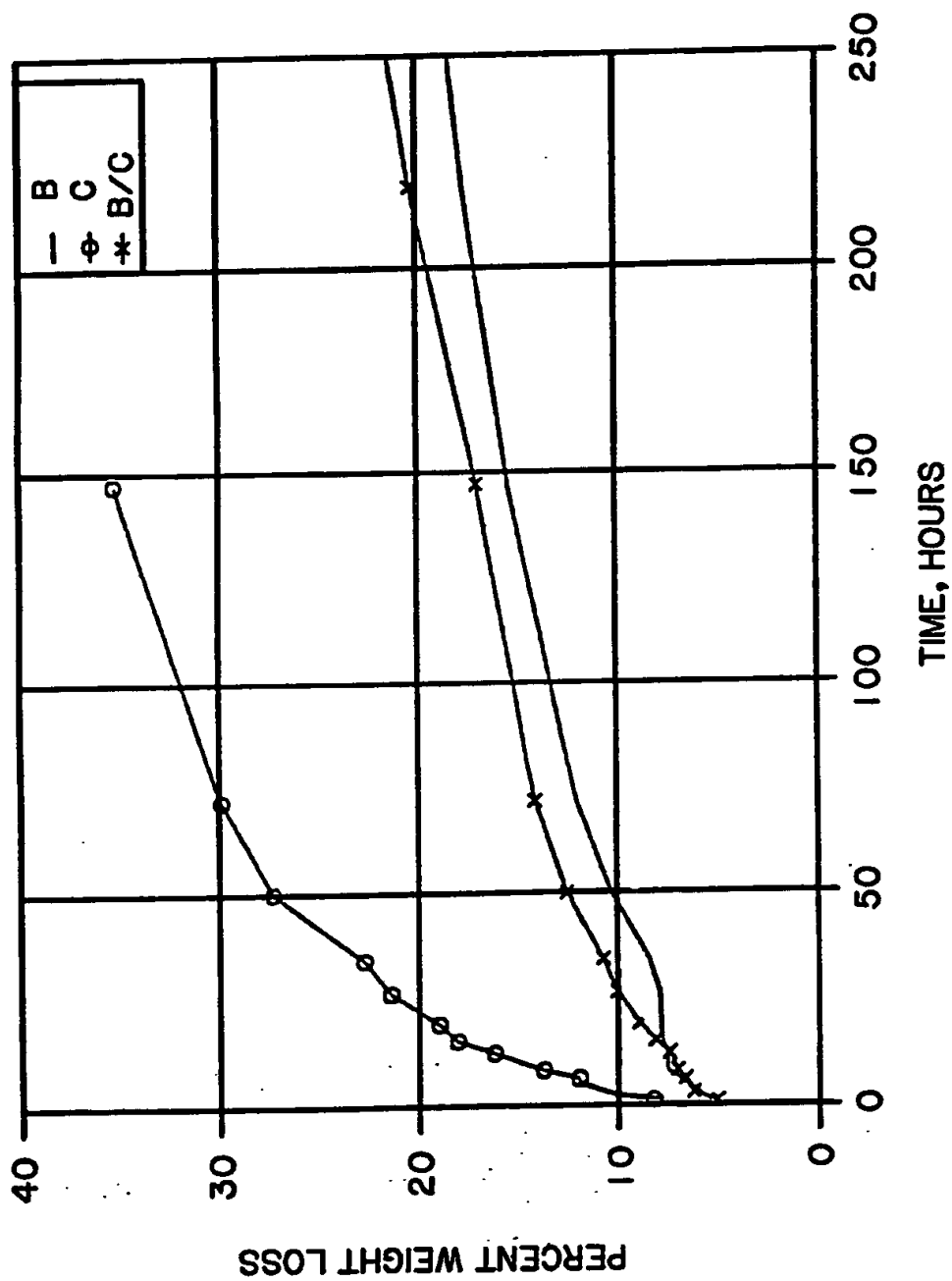
present in an amount of from 5% to 55%, based on the total weight of the coating composition.

22. A liquid coating composition as recited in claim 20 in which said silsesquioxane oligomer is present in an amount of from 8% to 30%, based on the total weight of the coating composition.

23. An optical glass fiber coated with a cured coating of the composition of claim 20.

1/5

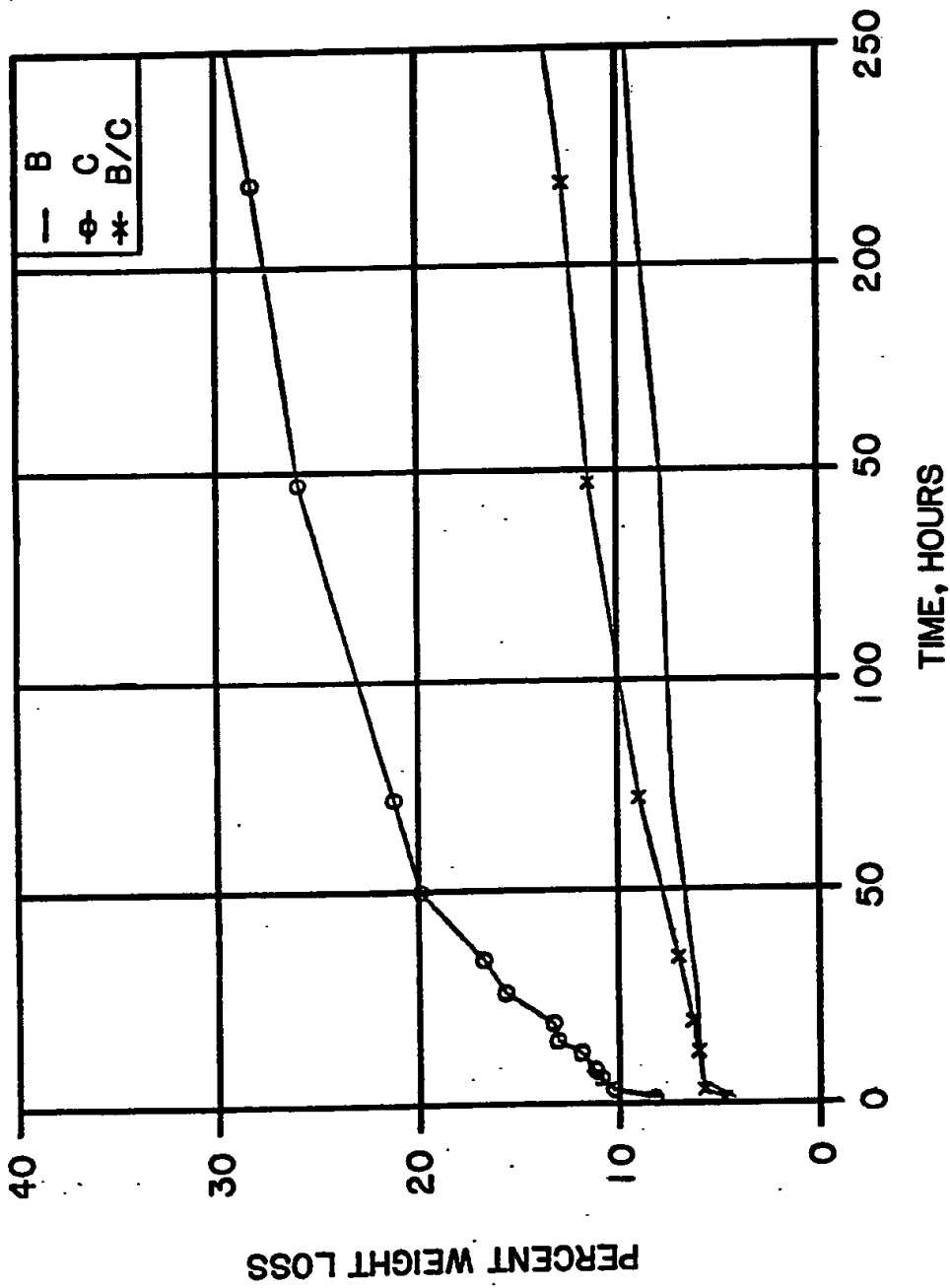
FIG. 1



SUBSTITUTE SHEET

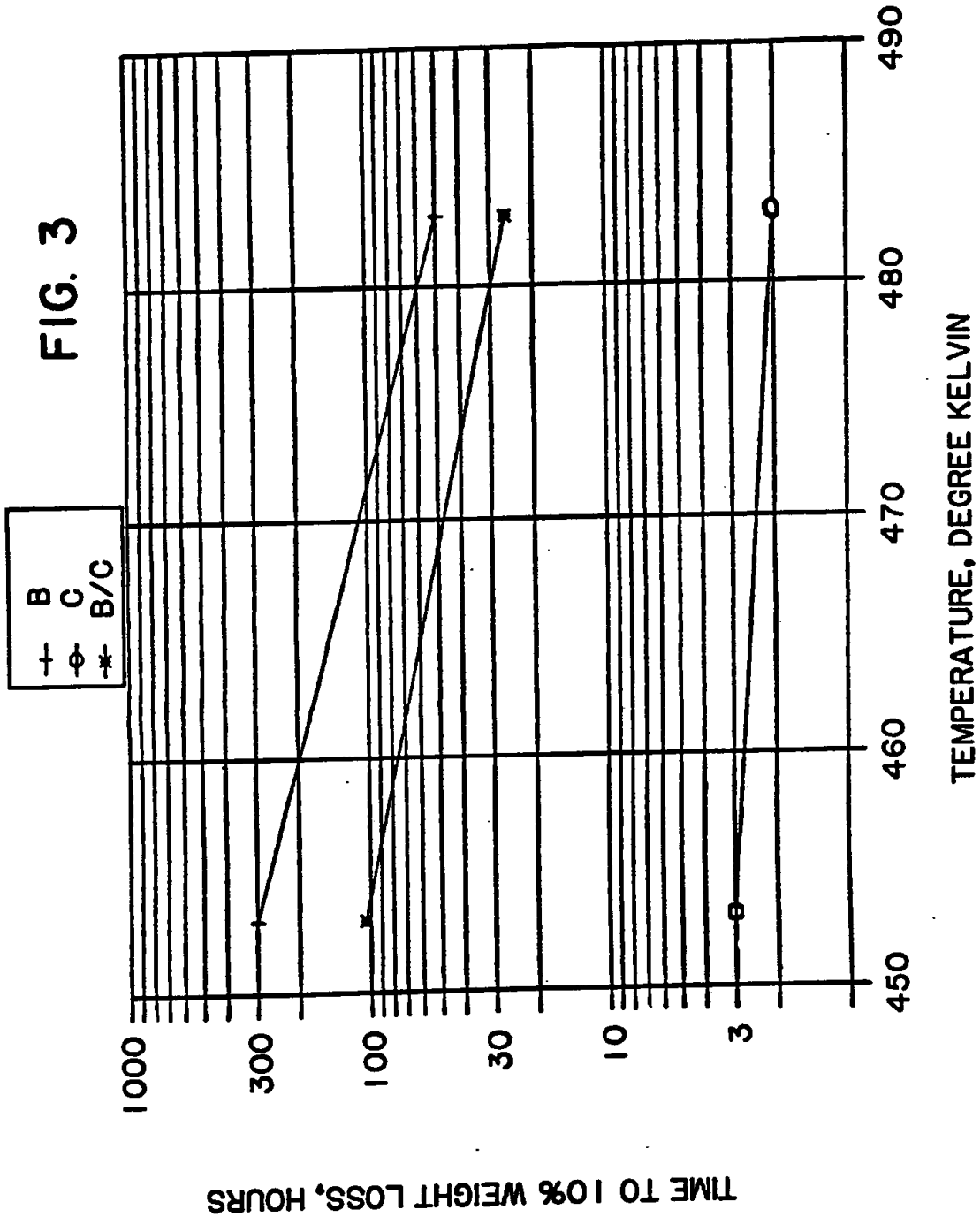
2/5

FIG. 2



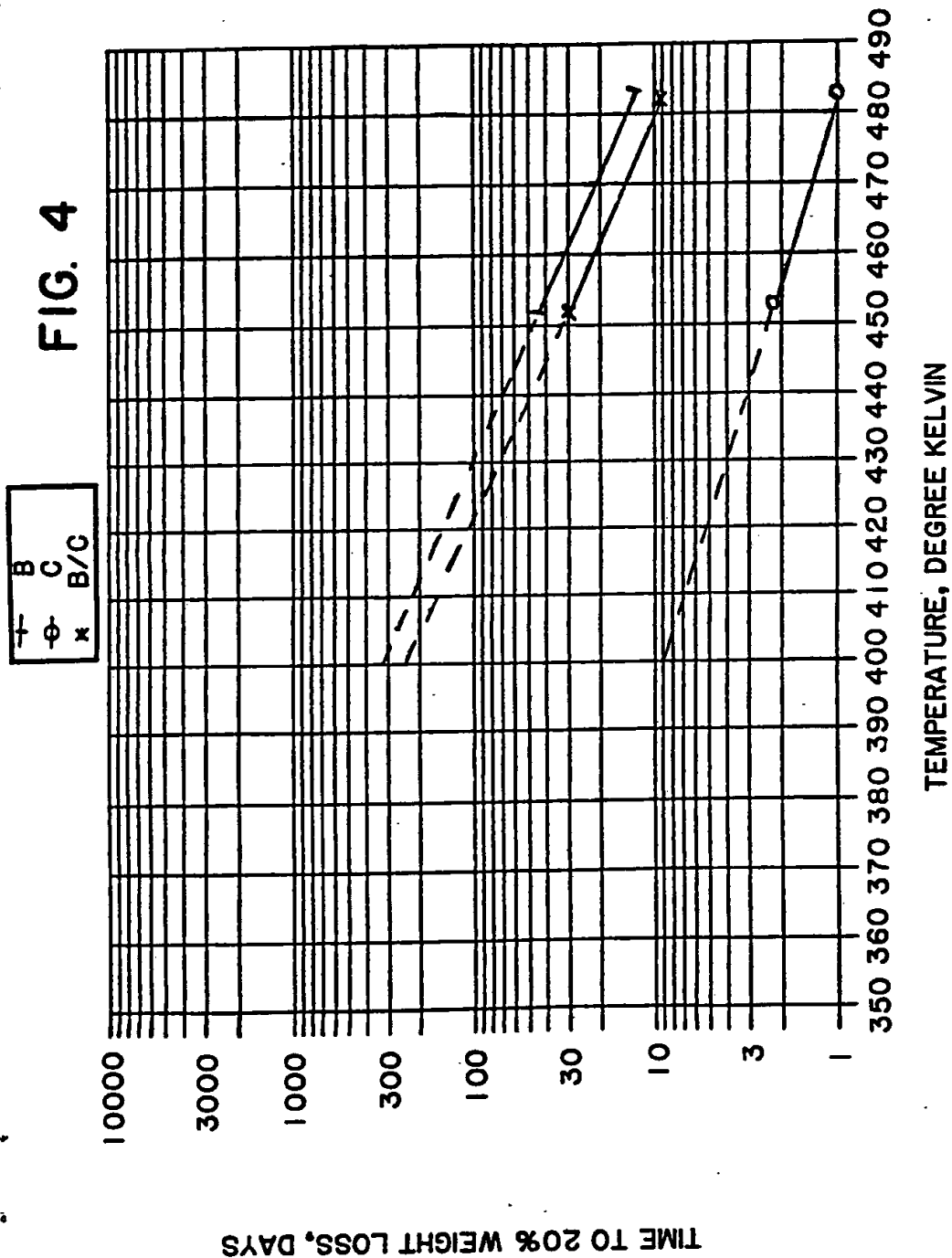
SUBSTITUTE SHEET

FIG. 3



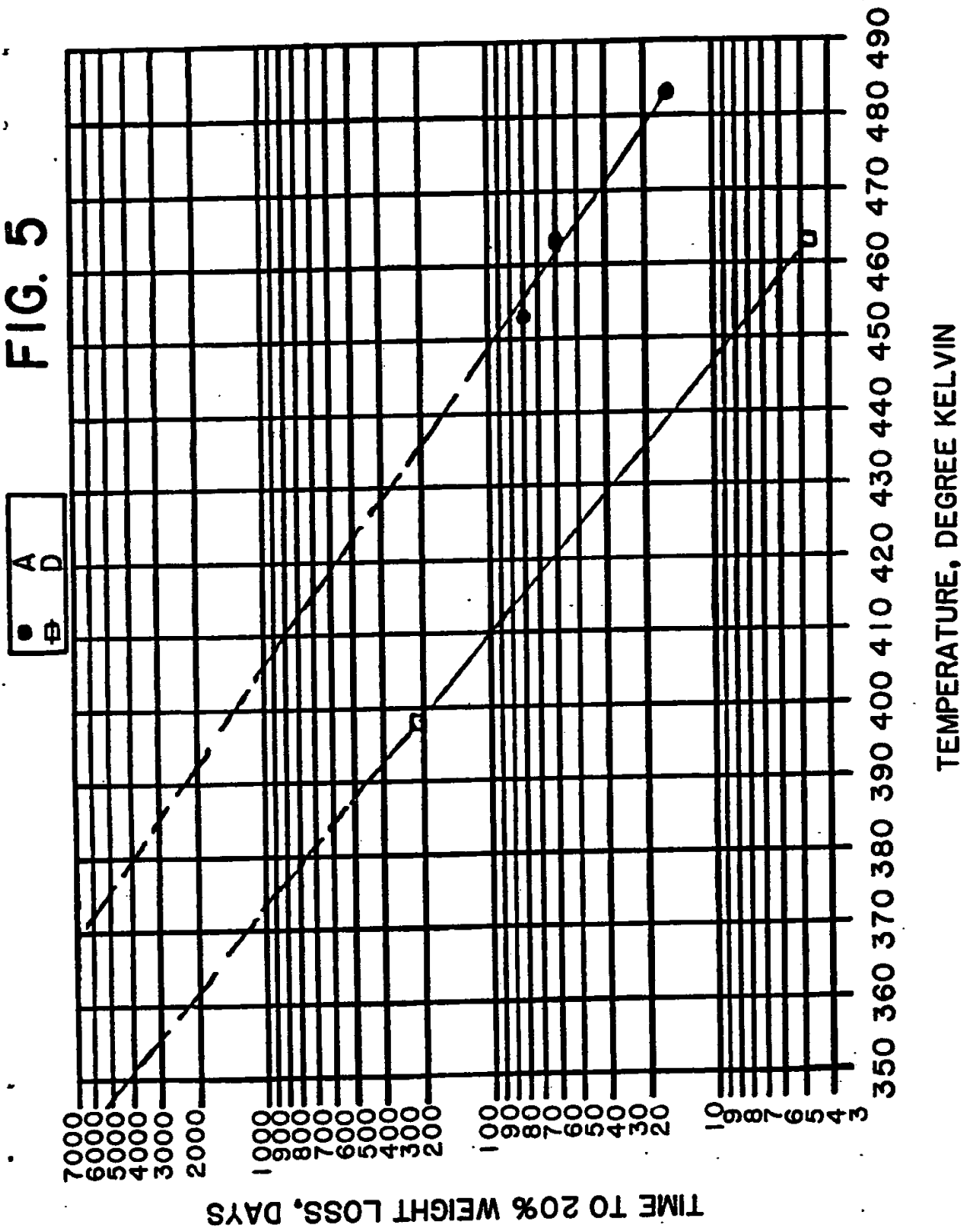
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FIG. 4



SUBSTITUTE SHEET

FIG. 5



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# INTERNATIONAL SEARCH REPORT

International Application No. **PCT/US89/04661**

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) * According to International Patent Classification (IPC) or to both National Classification and IPC <b>INT. CL<sup>5</sup> C08F, 30/08; B32B, 9/00</b> <b>U.S. CL 526/279; 428/391</b>														
<b>II. FIELDS SEARCHED</b> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched <sup>7</sup></div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 25%; border: 1px solid black;">Classification System</th> <th style="border: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: middle;">US</td> <td style="border: 1px solid black; text-align: center; vertical-align: middle;">526/279, 428/391</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup></div>			Classification System	Classification Symbols	US	526/279, 428/391								
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<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup></b> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%; border: 1px solid black;">Category <sup>10</sup></th> <th style="width: 60%; border: 1px solid black;">Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup></th> <th style="width: 30%; border: 1px solid black;">Relevant to Claim No. <sup>13</sup></th> </tr> </thead> <tbody> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top;">A, P</td> <td style="border: 1px solid black; vertical-align: top;">US, A 4,824,922, PUBLISHED 25 APRIL 1989, CHAPMAN, DECEASED. SEE ENTIRE DOCUMENT</td> <td style="border: 1px solid black; text-align: center; vertical-align: top;">1-23</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top;">A</td> <td style="border: 1px solid black; vertical-align: top;">US, A 4,780,515, PUBLISHED 25 OCTOBER 1988 DEICHERT. SEE ENTIRE DOCUMENT</td> <td style="border: 1px solid black; text-align: center; vertical-align: top;">1-23</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top;">A</td> <td style="border: 1px solid black; vertical-align: top;">US, A 4,419,505, PUBLISHED 6 DECEMBER 1983 RATKOWSKI, SEE ENTIRE DOCUMENT</td> <td style="border: 1px solid black; text-align: center; vertical-align: top;">1-23</td> </tr> </tbody> </table>			Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>	A, P	US, A 4,824,922, PUBLISHED 25 APRIL 1989, CHAPMAN, DECEASED. SEE ENTIRE DOCUMENT	1-23	A	US, A 4,780,515, PUBLISHED 25 OCTOBER 1988 DEICHERT. SEE ENTIRE DOCUMENT	1-23	A	US, A 4,419,505, PUBLISHED 6 DECEMBER 1983 RATKOWSKI, SEE ENTIRE DOCUMENT	1-23
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"d" document member of the same patent family</p> </div> </div>														
<b>IV. CERTIFICATION</b> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border: 1px solid black; padding: 5px;">           Date of the Actual Completion of the International Search  <b>29 JANUARY 1990</b> </td> <td style="width: 50%; border: 1px solid black; padding: 5px;">           Date of Mailing of this International Search Report  <b>05 MAR 1990</b> </td> </tr> <tr> <td style="border: 1px solid black; padding: 5px;">           International Searching Authority  <b>ISA/US</b> </td> <td style="border: 1px solid black; padding: 5px;">           Signature of Authorized Officer    <b>ALEX H. WALKER</b> </td> </tr> </table>			Date of the Actual Completion of the International Search <b>29 JANUARY 1990</b>	Date of Mailing of this International Search Report <b>05 MAR 1990</b>	International Searching Authority <b>ISA/US</b>	Signature of Authorized Officer  <b>ALEX H. WALKER</b>								
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## FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE<sup>1</sup>

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers \_\_\_\_\_, because they relate to subject matter <sup>12</sup> not required to be searched by this Authority, namely:

2. ☐ Claim numbers \_\_\_\_\_, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out <sup>13</sup>, specifically:

3. ☐ Claim numbers \_\_\_\_\_, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING<sup>1</sup>

This International Searching Authority found multiple inventions in this international application as follows:

GROUP I, CLAIMS 1-7, DRAWN TO POLYHYDROXY TERMINATED SILSESQUOXANE-HYDROXYFUNCTIONAL ETHYLENICALLY UNSATURATED MONOMER OLIGOMER.

GROUP II, CLAIMS 8, 9, 11, 13-16, 18 AND 20-22, DRAWN TO OLIGOMER-ETHYLENICALLY REACTIVE DILUENT LIQUID COMPOSITION. \*\*

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

## Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☒ No protest accompanied the payment of additional search fees.



\*\*

GROUP III, CLAIMS 10, 12, 17, 19 AND 23, DRAWN TO OPTICAL FIBERS  
COATED WITH CURED LIQUID COMPOSITION.